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CHEMICAL EQUILIBRIUM CODE WITH COMPRESSIBILITY FOR ABLATION AND EROSION CALCULATIONS

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13. ABSTRACT *(Maximum 200 words)*

A version of the LeRC CET chemical equilibrium code, which includes B_a value calculations for thermochemical erosion, was modified to include nonideal gas effects. The compressibility models that were added to the code were the BKW, Corner/Lennard-Jones Potential (LJP), and NBS models. Compressibility effects on species production for a variety of gun propellants were computed. These results were compared to the standard BLAKE code and were in agreement within the repeatability of the BLAKE code results. The effects of compressibility on values of the erosion rate blowing parameter, B_a, and hot wall/gas enthalpy, h_{gw}, were computed.

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INTRODUCTION

The diffusion limited chemical equilibrium combustion assumption is an important limit case for computing the chemical attack of reacting gases with a solid wall. Stated simply, this assumption means that if the reacting gas can get to the wall, it will react completely with the wall material to produce equilibrium products. If the further assumption of complete similarity between heat and mass transfer is made, i.e., unity Lewis number, then one of the driving potentials for heat transfer, the hot wall/gas phase enthalpy can also be computed using the results of a chemical equilibrium assumption. Taking the wall material as fuel and the combustion products of the gun propellant as oxidizer, then for a given O/F we would like to know the temperature at which all of the fuel is consumed. This temperature-O/F pair is often called the saturation point and gives us the blowing parameter B_a. The parameters, B_a and h_{gw}, are used in the following equations to define the mass erosion rate, m_g.

$$\rho_e U_e C_{h_o} = q_{cw} / (h_r - h_{gw}) \tag{1}$$

$$\rho_e U_e C_{h_B} = m_g / B_a \tag{2}$$

$$C_{h_B} / C_{h_o} = f(B_a, Mw) \tag{3}$$

where C_{h_B} and C_{h_o} are the Stanton numbers for mass and heat transfer.

Software and Engineering Associates, Inc. (SEA) of Carson City, NV, has included the calculation of B_a and h_{gw} in their version of the NASA LeRC CET (ref 1), code which is part of their Material Ablation Conduction Erosion (MACE) (ref 2) set of computer programs. The MACE code was developed for reentry and rocket motor ablation problems. In order to extend the code to gun tube erosion, the perfect gas assumption of the CET code had to be removed and a better equation-of-state implemented in the code. The BLAKE code (ref 3) was subsequently used in the gun community to calculate the equilibrium combustion products for gun propellants at high pressures, and there are several equations-of-state implemented in that code. The choice was then whether to put the blowing calculation from our version of CET into BLAKE or to put the equations-of-state from BLAKE into CET. Because of CET's more general chemistry set, it was decided to add the new equations-of-state to CET.

The BKW, Corner/Lennard-Jones Potential (LJP), and NBS equations-of-state were added to the MACE/CET codes and checked out by comparing the results with BLAKE calculations for the same chemical systems. Results from this comparison are presented in the verification section of this report. The effects of compressibility on B_a and h_{gw} for several propellant systems and wall materials are presented in the results section.

APPROACH

Equations-of-State

The general equation-of-state used here is the same as used in the BLAKE and Tiger codes (ref 4), that is:

$$P = \rho ZRT \tag{4}$$

where Z is the compressibility factor (1.0 for an ideal gas).

We shall limit our brief discussion of the calculation of Z to the Corner/LJP model, since that is the model most used from the BLAKE code. References 3 through 5 give more complete discussions of the various compressibility models.

The Corner/LJP model uses a truncated virial equation-of-state, that is

$$Z = [1 + \rho B(T) + \rho^2 C(T)] \tag{5}$$

However, the Corner model assumes that the second virial coefficient, C, is a constant and not a function of temperature. The details of the calculation of B and C are described in the BLAKE report and are not repeated here. The computation of the virial coefficients requires the Lennard-Jones parameters ε_i and σ_i for all the species considered in the calculation. We combined the Lennard-Jones parameter data from BLAKE, CET, and SPP (ref 5) to make as an extensive a set of data as possible. In the case of differences in the data, we took the values from BLAKE first, then CET, and lastly SPP. For molecules where there are no data, the values for nitrogen are assumed. This last assumption is the same as is used in BLAKE. Table 1 shows the species that are incorporated in the Compressible Chemical Equilibrium with Transport properties (CCET) code.

Table 1. Molecules with Lennard-Jones Parameters Considered in CCET

AL	ALCL	ALCL3	ALF	ALF3
ALN	ALO	ALS	AL2	AIR
AR	ASH3	B	BBR3	BCL
BCL2	BCL3	BF	BF2	BF3
BI3	BO	B(OCH3)3	B2	B2H6
B2O3	BE	BEBR2	BECL	BECL2
BEF	BEF2	BEI2	BE2	BR
BRF	BRF3	BRO	BR2	C
CBRF3	CBR4	CCL	CCLF3	CCL2
CCL2F2	CCL3	CCL3F	CCL4	CF
CF2	CF3	CF4	CH	CHBRCLF
CHBRCL2	CHBR3	CHCLF2	CHCL3	CHF3
CH2BRCL	CH2CLF	CH2CL2	CH2F2	CH2I2
CH3BR	CH3CL	CH3F	CH3I	CH3OH
CH4	CN	CO	COS	CO2
CP	CS	CS2	C2	C2H2
C2H4	C2H6	C2H5CL	C2H5OH	C2N2
CH3OCH3	CH2CHCH3	CH3CCH	CYCLO-C3H6	C3H8
N-C3H7OH	CH3COCH3	CH3COOCH3	N-C4H10	ISO-C4H10
C2H5OC2H5	CH3COOC2H5	N-C5H12	C(CH3)4	C6H6
C6H12	N-C6H14	CD	CL	CLCN
CLF	CLF3	CLO	CL2	F
FCN	F2	H	HBR	HCN
HCL	HF	HI	HS	H2
H2O	H2O2	H2S	HE	HG
HGBR2	HGCL2	HGI2	I	ICL
I2	KR	LI	LIBR	LICN
LICL	LIF	LII	LIO	LI2
LI2O	MG	MGCL	MGCL2	MGF
MGF2	MG2	N	NF3	NH
NH3	NO	NOCL	N2	N2O
NA	NABR	NACN	NACL	NAF
NAI	NAO	NAOH	NA2	NA2O
NE	O	OF	OF2	OH
O2	P	PCL	PCL3	PF
PF3	PH3	PN	PO	PS
P2	P4	S	SF6	SO
SO2	S2	S2F2	SI	SICL
SICL4	SIF	SIFCL3	SIF2CL2	SIF3CL
SIF4	SIH4	SIO	SIO2	SIS
SI2	SNBR4	SNCL4	UF6	XE
ZN				

Verification

The method of verification of the modifications made to the CCET code was to compare the new code with results from both the BLAKE and CET codes. Since the compressibility models were taken directly from the BLAKE code, the results should compare directly with that code. Comparisons with the CET code would establish that we had not broken the CCET code when we implemented the compressibility computations and would establish that all three codes computed the same result when compressibility was not a factor.

Figure 1 shows a comparison of selected species mole fractions as predicted by BLAKE and CCET for a pressure of 5000 atmospheres and a temperature range from 1000 to 5000°K. The upper set of symbols refers to the BLAKE numbers, and the lower set to the CCET numbers. Figures 2 and 3 show a comparison for compressibility and enthalpy. In Figure 2 the double valued point for the BLAKE compressibility stems from an apparent convergence tolerance problem when the results are computed going up a temperature isoline as compared to going down a temperature isoline. The input file listings for the BLAKE and CCET data are shown in Tables 2 and 3, respectively.

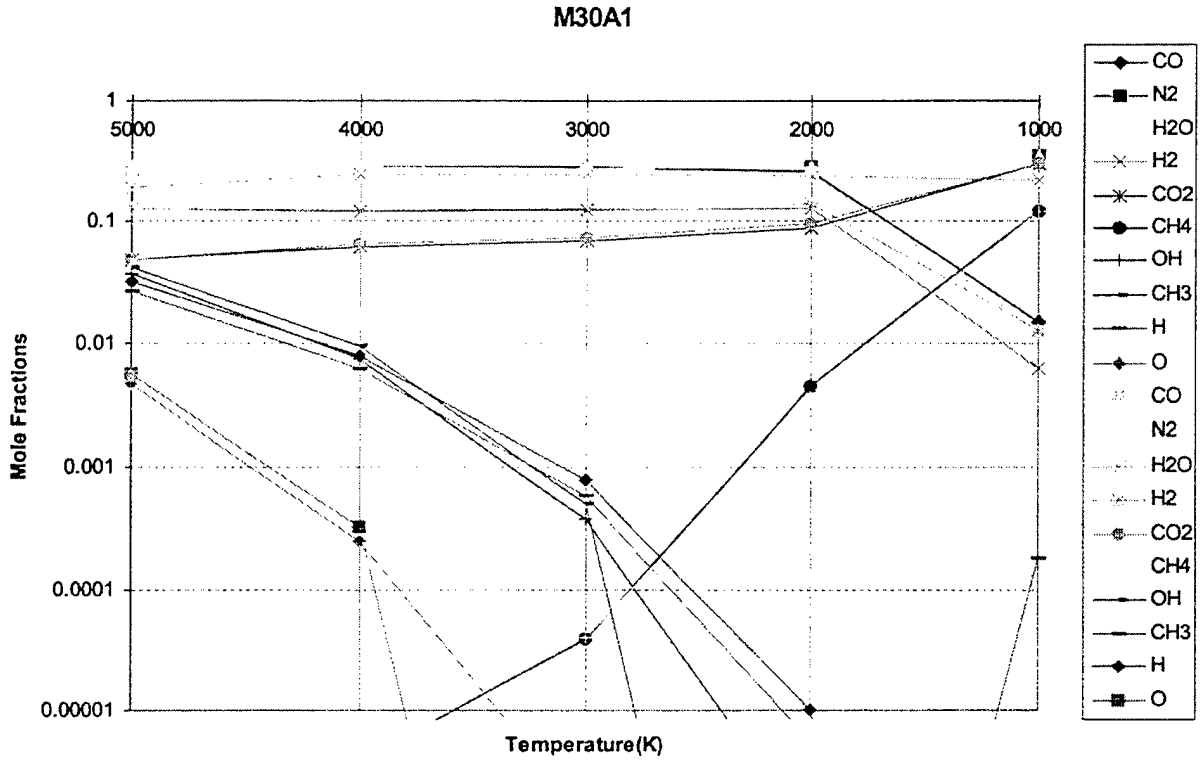

Figure 1. Comparison of BLAKE and CCET species mole fractions for M30A1 propellant.

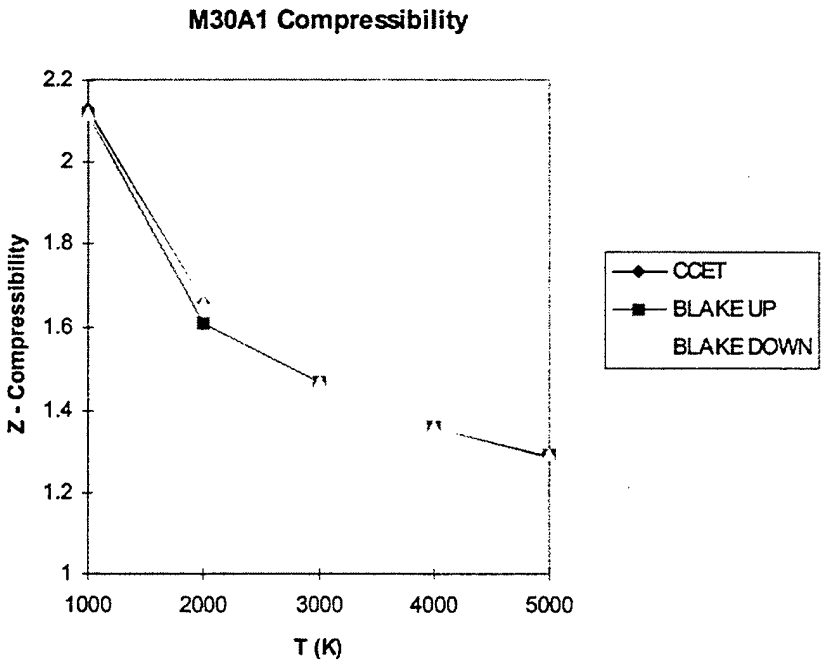

Figure 2. Comparison of BLAKE and CCET compressibility for M30A1 propellant.

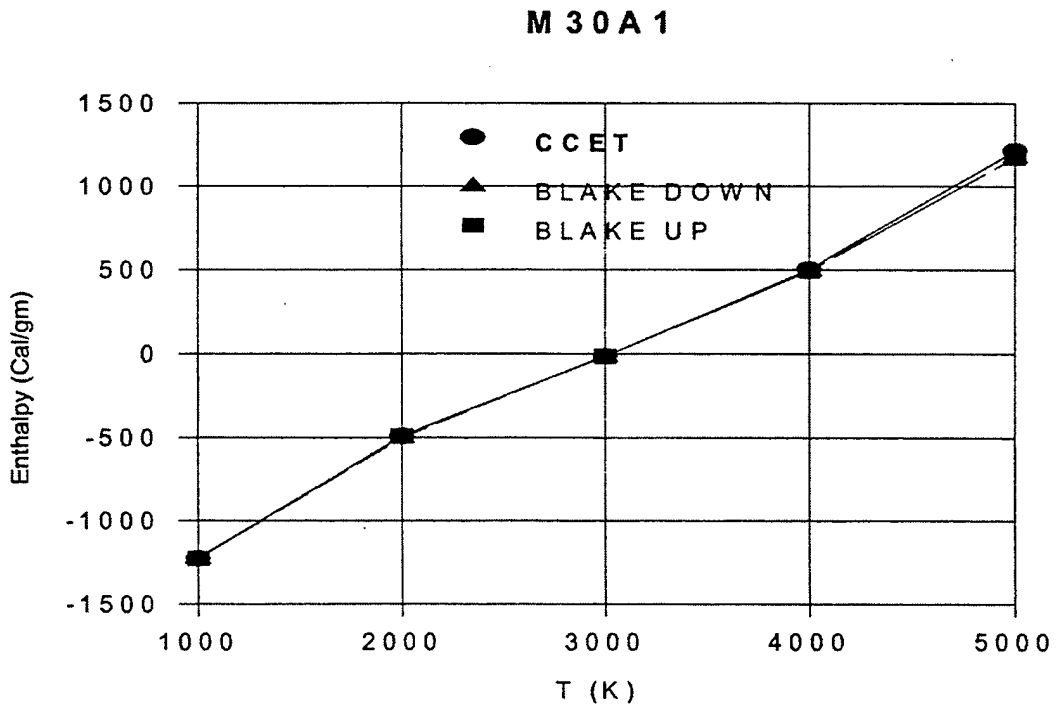

Figure 3. Comparison of BLAKE and CCET gas phase enthalpy for M30A1 propellant.

Table 2. Input File for CCET/M30A1 Propellant

```
#         Test of CCET versus Blake
#     a) Assigned temperature and pressure problem (tp = t).
#     b) Pressure is 5000 atm (atm = t).
#     c) Temperatures are given in degree K (t = ...).
#     d) M30A1 from LIBRARY cards.
#
 $DATA
  LIB = T, MOLE = F, LIBNAM = 'NC1260', 'NG', 'NQ', 'EC', 'KS', 'ALC', 'C',
                    MASMOL = 27.9, 22.42, 46.84, 1.49, 1.0, .25, .1,
 $END
```

OMIT	O2	C(GR)	C2N	C2H
OMIT	C2	CH2O	NO2	H2S
OMIT	S2O	SO2	K(S)	KOH(S)
OMIT	K2O	K2O2	KO2	HNO3
OMIT	C	CH	K2	N
OMIT	KCO(S)	KSO(S)	K2O(S)	NA2(S)
OMIT	C2H4	C2N2	C2H2	CH2
OMIT	HNO	HNO3	K2S(S)	
OMIT				

```
NAMELISTS
$CET
 LJP = T,
 TP = T,
 T = 1000, 2000, 3000, 4000, 5000
 P = 5000, ATM = T,
 $END
```

Table 3. Input File for BLAKE/M30A1 Propellant

```
TIT, M30A1 PROPELLANT UP
REJ, O2, C(S)
REJ, C2N, C2H, C2, CH2O, NO2, H2S, S2O, SO2, K$, KOH$, K2O,
REJ, K2O2, KO2, HNO3, C, CH, K2, N,
REJ, KCO$, KSO$, K2O$, NA2$
REJ, C2H4, C2N2, C2H2, CH2
REJ, HNO, HNO3
REJ,K2S$
ORD,N2,CO,H2O,KOH,HS
RET
CM2, NC1260, 27.90, NG, 22.42, NQ, 46.84, EC, 1.49,
  KS, 1.0, ALC, .25, C, .1
ISOline, P, 5000, T, 1000.,4, 5000.
STOP
```

The above comparison was repeated for M919 propellant for a pressure of 3000 atmospheres and temperatures from 1000 to 4000°K. The results were comparable to the M30A1 comparisons.

The final comparison was at one atmosphere using a stoichiometric mixture of ethanol and oxygen at a temperature of 3000°K. Comparisons between BLAKE, CCET, and CET were essentially identical.

RESULTS AND DISCUSSION

The purpose of this work was to develop an equilibrium code that would compute values of B_a and h_{gw} for use in thermochemical erosion studies, which include the effects of nonideal gas equations-of-state, that is, compressibility. Results were computed for the M30A1 propellant in conjunction with chromium with the compressibility option of CCET turned on and off for a pressure of 3000 atmospheres. The values for B_a were found to be essentially identical for the two cases and hence independent of compressibility. These results for the gas/wall enthalpy, h_{gw}, were significantly different and are shown in Figure 4.

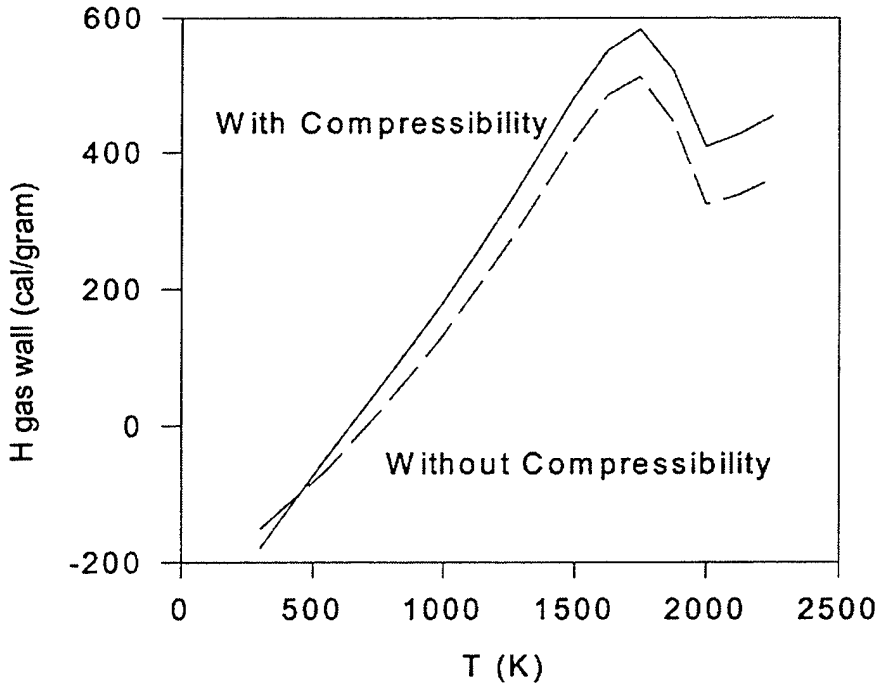

Figure 4. Enthalpy of the gas at the wall for M30A1 propellant.

These results show that the effects of compressibility are important when computing the heating and diffusion rates for thermochemical ablation/erosion for gun tube applications.

SUMMARY AND CONCLUSIONS

Modifications to extend the NASA LeRC CET to include compressibility effects have been demonstrated. The new code has been named the Compressible Chemical Equilibrium with Transport properties (CCET) code. Good agreement between the gun community's BLAKE code and the CCET has been shown.

The effect of compressibility on thermochemical erosion potentials, B_a and h_{gw}, has been calculated for two propellants, M30A1 and M919. It was concluded that compressibility is important in computing thermochemical erosion rates in gun tubes.

The compressibility models in BLAKE have been found to be adequate for internal ballistics computations. However, for other uses, we feel that more accurate models should be incorporated into the CCET. The calculation of diffusion coefficients and Schmit numbers for computed equilibrium conditions is also important for many applications and should be added to the CCET code.

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